1. ECN	197978
Proj. ECN	

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.		4. Date
Supplemental [] Direct Revision [X] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	J. B. Duncan, Environmental Engineering Support Group, H6-05, 372-0896		07/27/93

5. Project Title/No./Work Order No.	6. Bldg./Sys./Fac. No.	7. Impact Level
100-HR-3 Groundwater Treatability-740 Stevens Ctr.		3Q

8. Document Numbers Changed by this ECN (includes sheet no. and rev.)	9. Related ECN No(s).	10. Related PO No.
WHC-SD-EN-TC-003 Rev. 0	NA	NA

11a. Modification Work	11b. Work Package No.	11c. Modification Work Complete	11d. Restored to Original Condition (Temp. or Standby ECN only)
[X] Yes (fill out Blk. 11b) [] No (NA Blks. 11b, 11c, 11d)	P315B JBD	J. B. Duncan JBD Cog. Engineer Signature & Date	J. B. Duncan JBD Cog. Engineer Signature & Date

12. Description of Change

Complete Revision.

Complete revision to reflect comments from the regulatory agencies.

AUG 1993 RECEIVED EDMC

13a. Justification (mark one)	Criteria Change []	Design Improvement []	Environmental [X]
As-Found []	Facilitate Const. []	Const. Error/Omission []	Design Error/Omission []

13b. Justification Details

Comments were generated by regulatory agency contractors relating to kinetics, stoichiometry, and testing regimes.

14. Distribution (include name, MSIN, and no. of copies)

Central Files L8-04 (2)
EDMC H6-08 (2)
ERC H6-07 (1)

RELEASE STAMP

OFFICIAL RELEASE (11)
BY WHC
DATE AUG 06 1993
Station #12

A-7900-013-2 (06/92) GEF095

A-7900-013-1 (06/92)

15. Design Verification Required	16. Cost Impact				17. Schedule Impact (days)		
	ENGINEERING		CONSTRUCTION				
[] Yes	Additional	[] $	Additional	[] $	Improvement	[]	NA
[x] No NA	Savings	[] $	Savings	[] $	Delay	[]	

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

SDD/DD	[]	Seismic/Stress Analysis	[]	Tank Calibration Manual	[]
Functional Design Criteria	[]	Stress/Design Report	[]	Health Physics Procedure	[]
Operating Specification	[]	Interface Control Drawing	[]	Spares Multiple Unit Listing	[]
Criticality Specification	[]	Calibration Procedure	[]	Test Procedures/Specification	[]
Conceptual Design Report	[]	Installation Procedure	[]	Component Index	[]
Equipment Spec.	[]	Maintenance Procedure	[]	ASME Coded Item	[]
Const. Spec.	[]	Engineering Procedure	[]	Human Factor Consideration	[]
Procurement Spec.	[]	Operating Instruction	[]	Computer Software	[]
Vendor Information	[]	Operating Procedure	[]	Electric Circuit Schedule	[]
OM Manual	[]	Operational Safety Requirement	[]	ICRS Procedure	[]
FSAR/SAR	[]	IEFD Drawing	[]	Process Control Manual/Plan	[]
Safety Equipment List	[]	Cell Arrangement Drawing	[]	Process Flow Chart	[]
Radiation Work Permit	[]	Essential Material Specification	[]	Purchase Requisition	[]
Environmental Impact Statement	[]	Fac. Proc. Samp. Schedule	[]		[]
Environmental Report	[]	Inspection Plan	[]		[]
Environmental Permit	[]	Inventory Adjustment Request	[]		[]

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number Revision
NA		

20. Approvals

Signature	Date	Signature	Date
OPERATIONS AND ENGINEERING		ARCHITECT-ENGINEER	
Cog Engineer J. B. Duncan	7/28/93	PE	
Cog. Mgr. J. G. Woolard	7/21/93	QA	
QA G. S. Corrigan	7/28/93	Safety	
Safety		Design	
Security		Environ.	
Environ.		Other	
Projects/Programs			
Tank Waste Remediation System			
Facilities Operations		DEPARTMENT OF ENERGY	
Restoration & Remediation		Signature or Letter No.	
Operations & Support Services			
IRM		ADDITIONAL	
Other			

SUPPORTING DOCUMENT

	1. Total Pages 42

2. Title	3. Number	4. Rev No.
100-HR-3 Area Groundwater Treatment Tests for Ex Situ Removal of Chromate, Nitrate, and Uranium(VI) by Precipitation/Reduction and/or Ion Exchange	WHC-SD-EN-TC-003	1

5. Key Words	6. Author
precipitation, anion exchange, ferrous sulfate, soldium sulfide, disodium hydrogen phosphate, resin	Name: J. B. Duncan

APPROVED FOR
PUBLIC RELEASE

V. Birkland 8/4/93

Signature

Organization/Charge Code 81340/P71AA

7. Abstract

WHC, 1993, *100-HR-3 Area Groundwater Treatment Tests for Ex Situ Removal of Chromate, Nitrate, and Uranium(VI) by Precipitation/Reduction and/or Ion Exchange*, WHC-SD-EN-TC-003, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

10.	RELEASE STAMP

OFFICIAL RELEASE ⑪
BY WHC
DATE AUG 06 1993
Statia #12

9. Impact Level 3Q

THIS PAGE INTENTIONALLY
LEFT BLANK

INFORMATION RELEASE REQUEST

Reference:
WHC-CM-3-4

Complete for all Types of Release

Purpose

[] Speech or Presentation
  [] Full Paper   (Check
  [] Summary   only one suffix)
  [] Abstract
  [] Visual Aid
[] Speakers Bureau
[] Poster Session
[] Videotape

[] Reference
[X] Technical Report
[] Thesis or Dissertation
[] Manual
[] Brochure/Flier
[] Software/Database
[] Controlled Document
[] Other

ID Number (include revision, volume, etc.)

WHC-SD-EN-TC-003, Rev. 1

List attachments.

N/A

Date Release Required

July 30, 1993

Title 100-HR-3 Area Groundwater Treatment Tests for Ex Situ Removal of Chromate, Nitrate, and Uranium(VI) by Precipitation/Reduction and/or Ion Exchange

Unclassified Category

UC-

Impact Level 3Q

New or novel (patentable) subject matter? [X] No [] Yes
If "Yes", has disclosure been submitted by WHC or other company?
[] No [] Yes Disclosure No(s).

Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions?
[X] No [] Yes (Identify)

Copyrights? [X] No [] Yes
If "Yes", has written permission been granted?
[] No [] Yes (Attach Permission)

Trademarks?
[X] No [] Yes (Identify)

Complete for Speech or Presentation

Title of Conference or Meeting
N/A

Group or Society Sponsoring

Date(s) of Conference or Meeting | City/State

Will proceedings be published? [] Yes [] No
Will material be handed out? [] Yes [] No

Title of Journal

CHECKLIST FOR SIGNATORIES

Review Required per WHC-CM-3-4	Yes	No	Reviewer - Signature Indicates Approval Name (printed)	Signature	Date
Classification/Unclassified Controlled Nuclear Information	[]	[X]			
Patent - General Counsel	[X]	[]	S. Berglin	per 2/4/93	7/23/93
Legal - General Counsel	[X]	[]	S. Berglin	OGC memo	
Applied Technology/Export Controlled Information or International Program	[]	[X]			
WHC Program/Project	[]	[X]			
Communications	[]	[X]			
RL Program/Project	[X]	[X]			
Publication Services	[X]	[]	L.A. Brown	L.A. Brown	7/23/93
Other Program/Project	[]	[X]			

Information conforms to all applicable requirements. The above information is certified to be correct.

	Yes	No	INFORMATION RELEASE ADMINISTRATION APPROVAL STAMP
References Available to Intended Audience	[X]	[]	Stamp is required before release. Release is contingent upon resolution of mandatory comments.
Transmit to DOE-HQ/Office of Scientific and Technical Information	[]	[X]	

Author/Requestor (Printed/Signature) | Date

J. B. Duncan   Jane B. Du...   August 2, 1993

Intended Audience

[] Internal   [] Sponsor   [X] External

Responsible Manager (Printed/Signature) | Date

J. G. Woolard   JG Woolard   8/2/93

Date Cancelled | Date Disapproved

THIS PAGE INTENTIONALLY
LEFT BLANK

(2) Title

Test Procedures - 100 Area Groundwater Treatability Test for Ex-Situ Removal of Chromate, Nitrate, and Uranium (UI)

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release		
		(5) Cog. Engr.	(6) Cog. Mgr.	Date
Rev 0	(7) EDT 142064	JB Duncan	JG Woolard 5/22/93	7/29/9
Rev 1 RS	Complete Revision	JB Duncan	JG Woolard 7/27/93	7/29/9

9 3 1 3 0 2 3 2 0 3 5

A-7320-005 (08/91) WEF168

THIS PAGE INTENTIONALLY LEFT BLANK

CONTENTS

APPENDIXES:

TABLES:

1.0 INTRODUCTION

These test procedures describe laboratory studies proposed to investigate ex situ methods to remove chromate, nitrate, and uranium from contaminated Hanford Site groundwaters. Uranium is the major species contributing to the elevated alpha levels. By removing the uranium, the alpha levels will be significantly reduced at the uranium concentration found in the 100-HR-3 Groundwater Operable Unit. Also, if uranium is removed, the beta-emitting daughters (thorium and protactinium) are also quickly removed, as they have half-lives of 24 days and 6 hours, respectively. Furthermore, all subsequent daughters will be prevented. It is important to note that technetium is not addressed because it has a drinking water limit (5,000 pCi/L) higher than the levels found in most 100-HR-3 wells. Also, because technetium exists as pertechnetate, there is a high probability that it will be removed in a serendipitous manner. The technologies to be investigated, chemical precipitation or coprecipitation to remove chromate and uranium and anion exchange to remove chromate, uranium and nitrate, are identified in the *100-HR-3 Groundwater Treatability Test Plan* (DOE-RL 1992a). Precipitation is not expected to remove nitrate from solution.

Precipitation-based removal of chromate (as well as associated metals such as zinc, nickel, cadmium, and copper) from plating bath wastes has been tested and implemented (Beller et al. 1989). The process utilizes sodium sulfide and ferrous sulfate to first reduce chromate to chromate(III) and then to coprecipitate the reduced chromate with the resulting ferric hydroxide/ferric sulfide. The successful results of the implementation of this approach corroborate Westinghouse Hanford Company (WHC) laboratory studies in which sodium sulfide and ferrous sulfate were used separately in the reduction and precipitation from solution of chromate (Thornton et al. 1991). The method proposed by Beller et al. (1989) will be tested for removal of chromate from Hanford Site groundwater. The possible reduction/precipitation and retention of uranium by this technique also may occur and will be tested. Removal of uranium from Hanford Site groundwaters and wastewaters by ferric hydroxide coprecipitation has been tested with promising results (Hodgson 1988).

Carrier precipitation of uranium by calcium hydrogen phosphate (brushite) has been implemented in treating uranium fuel fabrication plant waste solutions (Muller 1984). Thus, simple addition of disodium hydrogen phosphate to precipitate brushite from the contained calcium ion naturally present in the Hanford Site groundwater will be tested for its efficacy in removing uranium. Experiments may show, however, that additional calcium ion, introduced as calcium chloride solution to the groundwater, is required to provide sufficient precipitate to carry uranium. The incidental removal of chromate from solution by coprecipitation with brushite also will be checked.

The precipitation method(s) for chromate and uranium removal from the groundwater may be used in conjunction with a biodenitrification method for nitrate removal. Thus, an important subsequent objective shall be the successful integration of the proposed precipitation and biodenitrification steps.

Strong-base anion exchange has been used in separate approaches to remove chroamte from corrosion inhibition solutions used in water-cooled heat exchange equipment and to remove nitrate from nitrate-polluted waters

1

(Kirk-Othmer 1981a). Strong-base anion exchange also has been used successfully in uranium milling operations (Benedict et al. 1981) as well as to remove uranium from contaminated Hanford Site groundwaters (Delegard et al. 1986).

In the proposed tests, three strong-base anion exchange resins will be tested for their efficiency and capacity in removing the three contaminants (chromate, uranium, and nitrate) from Hanford Site groundwater. Based on these tests, one, or possibly two, of the resins will be evaluated further for breakthrough capacity and regeneration characteristics. The three resins were selected for these applications on the recommendations of the resin manufacturers, Rohm and Haas Company and Dow Chemical Company.

2.0 SCOPE AND OBJECTIVES

These test procedures identify all tests to be performed and the associated testing parameters, schedules, and data collection requirements. Included are the experimental designs and general procedures to be used in preparing the solutions and assembling the test apparatus and the types of data to be recorded during the tests. Also identified are the organizations responsible for the several tasks involved in this work and the locations where the laboratory work will be performed. The objectives of the treatment tests are summarized in Table 1 and in the treatibility test plan (DOE-RL 1992a).

Table 1. Test Objectives.

Reduction/precipitation	Determine physical conditions and removal chemistry, and associated sludge generation quantities; determine reaction rates; determine effects of feed variability and presence of other contaminants; determine sludge characteristics, stabilization, and filtration qualities; determine if biodenitri- fication hinders precipitation or reduction reactions; determine co-removal of uranium
Ion exchange	Determine pretreatment requirements; determine resin(s) efficacy; determine falloff in loading after multiple cycles; determine resin regeneration requirements, and waste volumes and compositions

3.0 REQUIREMENTS

The safety, quality assurance (QA), reporting, and equipment requirements, as well as the project schedule, are provided in the following sections.

3.1 SAFETY REQUIREMENTS

Laboratory personnel will comply with the WHC Chemical Hygiene Program (WHC 1992) and other internal WHC industrial safety requirements. Special safety requirements identified in this test plan are associated with the use of solutions, solids, and labware containing solutions of chromate and uranium. Handling of these materials will be conducted in fume hoods to eliminate inhalation hazards. The operator will wear rubber gloves as protection against absorption pathways through the skin.

Material Safety Data Sheets (MSDS) shall be used as a primary reference during the handling of the chemical materials used in the tests. The MSDS numbers for the chemical materials identified in the testing activities are listed below.

Chemical	MSDS No.
Sodium chromate	1486
Uranyl nitrate	2783
Sodium nitrate	1506
Ferrous sulfate	2871
Sodium sulfide	1512
Disodium hydrogen phosphate	1886
Sodium chloride	1485
Sodium bicarbonate	1480
Calcium chloride	1087
Silver nitrate	1472

Resin	MSDS No.
IRA-402®*, Rohm and Haas	13688
IRA-410®**, Rohm and Haas	13538
Dowex 21K®**, Dow	10847

---

*A trademark of the Rohm and Haas Company.

**A trademark of Dow Chemical Company.

3.2 QUALITY ASSURANCE/QUALITY CONTROL AND DATA
RECORDING REQUIREMENTS

The activities undertaken in this test procedure shall be performed in accordance with the quality assurance program plan for the processing and analytical laboratories (WHC 1993). The quality assurance program plan is written to ensure compliance with the U.S. Department of Energy (DOE), Richland Operations Office (RL) requirements for environmental restoration work (DOE-RL 1992b).

All data collected during the course of these testing activities shall be recorded on approved data sheets or in controlled laboratory notebooks issued through WHC Document Control. Data sheets shall be affixed into the laboratory notebooks. These records shall be reviewed and approved by supervisory personnel within the performing organizations in a timely manner and shall be organized and stored under controlled conditions maintained by the performing organizations. These records shall include identification of all key measuring devices and associated calibration records. Chain-of-custody records for samples and analytical records associated with samples also shall be maintained and stored in a controlled manner. Data and sample control activities shall be performed in accordance with QA requirements of the performing organizations and in a manner appropriate for an Impact Level 3Q developmental effort (i.e., in a manner consistent with standard laboratory practices with QA review). These records shall be available for review by representatives of the WHC Environmental Engineering Group.

Analyses of the chromium- , uranium- , and nitrate-containing solutions utilized in this work shall be obtained through WHC analytical laboratories to verify the concentrations of chromium, uranium, and nitrate being used and to check the stability of the solutions. A sample of the Hanford groundwater used in these experiments shall also be analyzed for all cations by inductively coupled plasma spectrometry (ICP) and for anions by ion chromatography (IC), total organic carbon (TOC), and total inorganic carbon (TIC), which is carbonate, uranium, chromate, and pH. NOTE: The schedule for testing and the availability of the laboratory for analyses (predicated on existing schedules) may require tests to be performed at the laboratory that has the capacity. All QA/QC for any analyses will be identical for each laboratory at which the analyses are performed.

The reference numbers for the procedures used for chemical analyses are presented in Table 2. As these analyses may be performed at either the 222-S or PUREX laboratories, method numbers for both laboratories are given where appropriate. The methods listed in Table 2 will also give values for calcium, magnesium, carbonate, hardness, dissolved solids, and those tests conducive to standard water analyses.

Table 2. Chemical Analyses.

Analyte(s)	Method	Title	Minimum Detection Limit[a]	Performance level[b]
Cations (ICP)	LA-505-151	ICP Emission Spectrometer Method for Trace Element Analysis of water and waste	50 ppb	100 ppb Cr(VI)
Total chromium	LA-505-151 LA-505-241	ICP Emission Spectrometer Method for Trace Element Analysis of water and waste	50 ppb	100 ppb Cr(VI)
Chromium (VI)	LA-265-101	Spectrophotometric determination of Cr(VI)	25 ppb	80 ppb Cr(VI)
Anion (IC)	LA-533-105 LA-533-201	Anion analysis on Dionex Model 4000i[c]	10,000 ppb	45,000 ppb nitrate
Nitrate	LA-533-105 LA-533-201	Anion analysis on Dionex Model 4000i[c]	10,000 ppb	45,000 ppb nitrate
Uranium	LA-925-106	Determination of uranium by laser fluorimetry	1 ppb uranium	15 pCi/L gross alpha = 22 ppb uranium[d]
Total organic carbon	LA-344-105	Determination of carbon in solutions by combustion and coulometry	N/A	N/A
Total inorganic carbon	LA-622-102	Determination of carbonate/carbon or total organic carbon in solutions by coulometry	N/A	N/A
Total alpha and total beta	LA-508-101	Alpha and beta in liquid sample	5 pCi/L gross alpha, +/-50%; 10 pCi/L gross beta, +/-50%	15 pCi/L gross alpha 40 pCi/L gross beta
pH	LA-212-102	Determination of pH direct measurement	N/A	N/A

IC = ion chromatography.
ICP = inductively coupled plasma spectrometry.
N/A = not applicable.
[a]The precision and accuracy goals for all analyses will be 25% relative percent difference and 75% to 125% recovery, respectively. Representativeness is addressed by using solutions that have concentrations that are similar to either regulatory performance levels or contamination levels found in 100 Area groundwaters. Comparability of the data generated will be discussed, where appropriate, in the final report.
[b]Values from DOE (1992a).
[c]A trademark of the Dionex Corporation.
[d]Based on natural uranium.

3.3 REPORTING REQUIREMENTS

Original or high-quality copies of all records generated during the testing activities shall be assembled as a project data file by the performing organization, the WHC Process Chemistry Laboratory (PCL). These data packages shall be transmitted to the WHC Environmental Engineering Group and shall be accompanied by letter reports describing the work performed. The results and conclusions obtained from the activities described in this test procedure shall be compiled and documented in a project report coauthored by representatives of the WHC Environmental Engineering Group and PCL. This report shall be completed and delivered to WHC management by September 2, 1993.

3.4 SCHEDULE

The schedule for these tasks has been defined in the treatability test plan (DOE-RL 1992a). The points in the schedule pertaining to the laboratory activities defined in this test procedure are summarized in Appendix A.

3.5 EQUIPMENT

Ordinary laboratory equipment will be used, which includes but is not limited to centrifuges, stirrers, ion exchange columns, pumps, centrifuge tubes, and pipetters.

4.0 PROCEDURE OVERVIEW

4.1 TREATMENT PARAMETER SELECTIONS

The goal of the tests described in this test procedure is to determine the efficacy of precipitation-based techniques in the removal of chromium and uranium and the efficacy of anion exchange in the removal of chromium, uranium, and nitrate from Hanford Site groundwater. Steps involved in these activities include the following.

Precipitation Tests

1. Collect uncontaminated Hanford Site groundwater and analyze for the analytes listed in Table 2 (except gross alpha and gross beta)

2. Spike chromate, uranium, and nitrate into the uncontaminated groundwater, and mix thoroughly, in varying concentrations according to the statistical plan (Section 4.2)

3. Aliquot spiked groundwater and introduce precipitation agents, noting temperature

4. Mix treated groundwater samples thoroughly

5. Collect, filter, and analyze groundwater samples for chromate, total chromium, nitrate, and uranium, and analyze filter cake for volume and percent water

6. Integrate and interpret results and select most effective precipitation agent

7. Treat fully spiked groundwater with selected precipitation agent; collect, filter, and analyze groundwater samples for chromate, total chromium, nitrate, and uranium as a function of time; and analyze filter cake for volume and percent water

8. Integrate and interpret results.

6

Anion Exchange Tests

1. Collect uncontaminated Hanford Site groundwater and analyze for the analytes listed in Table 2 (except for gross alpha and gross beta)

2. Spike chromate, uranium, and nitrate into the uncontaminated groundwater in varying concentrations, and mix thoroughly according to the statistical plan

3. Condition resins to chloride form using sodium chloride solution

4. Aliquot spiked groundwater and introduce conditioned resins

5. Agitate groundwater/resin samples thoroughly for 30 min

6. Centrifuge groundwater/resin mixture, collect supernatant solution, and analyze groundwater samples for chromate, total chromium, uranium, and nitrate

7. Integrate and interpret results and select most effective resin

8. Perform breakthrough test on selected resin by pumping fully spiked groundwater through a resin column and collecting, filtering, and analyzing effluent groundwater samples as a function of throughput volume

9. Perform load/elute cycling tests of selected resin to monitor resin stability

10. Integrate and interpret results.

4.2 CONFIRMATORY TESTING

Following the precipitation and anion exchange tests previously described, confirmatory tests will be run using contaminated groundwaters obtained from wells 199-D5-15 (high chromium and low nitrate and radionuclides), 199-H4-4 (high nitrate and radionuclides but low chromium), 199-H4-12 (low nitrate, chromium, and radionuclide contamination), and 199-H4-12A (high in nitrate, gross alpha and beta, low in chrome). These waters have been specified for testing (DOE-RL 1992a) and will be examined using the following:

*   Selected precipitating agents

*   Anion exchange resins

*   Treatment conditions delineated in the following sections.

The confirmatory testing will also include the following:

- The use of groundwater after the biodenitrification tests and/or by the kinetics (precipitation or breakthrough ion exchange) tests

- Sulfate analysis

- Gross alpha and gross beta analyses (these require large volumes that are only available during the confirmatory testing)

- pH before and after treatment regimes

- Gravity settling test (for flocculation basin parameters).

4.3 RESPONSIBILITIES

The WHC Environmental Engineering Group shall be responsible for project management activities and for step 1 in both precipitation and anion exchange tests. The WHC Environmental Engineering Group shall also be jointly responsible with the WHC PCL in the integration and interpretation of results (steps 6 and 8 in the precipitation tests and steps 7 and 10 in the anion exchange tests). Personnel in the WHC PCL shall perform the experimentation and shall submit the samples to the WHC analytical laboratories for analysis.

Personnel safety must be considered in handling the moderately hazardous materials involved in these tests. Protective rubber gloves shall be worn whenever working with chromium- or uranium-bearing materials or equipment. Any experimentation involving chromium or uranium must be conducted in a hood. All laboratory tests will be conducted at the 222-S laboratory. Analytical work will be conducted at 222-S/202-A (PUREX) laboratories.

4.4 PREPARATION OF SPIKED HANFORD SITE GROUNDWATER

Artificially contaminated Hanford Site groundwater shall be prepared by spiking uncontaminated Hanford Site groundwater with solutions containing sodium chromate, uranyl nitrate, and sodium nitrate. The well identified for this is H3-2C because it lacked contamination (therefore, known spikes are able to be added) and the well resides in the 100-H Area. The concentrations of spike contaminant in the test groundwaters are given in Table 3.

The spiked groundwaters will be used in both the precipitation and anion exchange tests. For both sets of tests, two-level, full-factorial experimental designs will be performed in which chromate, uranium, and nitrate concentrations are the test factors run at high and low values. Thus, 2 x 2 x 2 = 8 different solution compositions will be prepared and used as separate samples (i.e., no compositing).

The high spike level is set to include all credible levels of uranium and to provide a separation of contamination levels, thus allowing effects to be determined more clearly.

Table 3. Concentrations of Spike Contaminants in the Test Solutions.

Solution number	Concentration (ppb)		
	Chromate	Uranium	Nitrate
1	2,000	800	200,000
2	2,000	800	2,000
3	2,000	40	200,000
4	2,000	40	2,000
5	50	800	200,000
6	50	800	2,000
7	50	40	200,000
8	50	40	2,000

The lowest concentrations of chromium and uranium in these spiked groundwater solutions are values near the maximum contaminant level (MCL) for those species. The lowest value for nitrate was chosen to reflect a trace value for nitrate. The MCL for nitrate in drinking water is 45,000 ppb. This concentration is equivalent to about 0.73 mmol/L and is comparable with the concentrations of the anionic species naturally occurring in the Hanford Site groundwater: bicarbonate (2 mmol/L), chloride (0.1 mmol/L), and sulfate (0.1 mmol/L). Therefore, nitrate at the 45,000-ppb MCL level cannot be considered a chemically trace constituent in the groundwater, whereas chromate and uranium at their respective MCL levels can.

To assess accurately the effects of nitrate on chromate and uranium treatment tests as well as not overwhelm the groundwater chemistry, the lower level of nitrate was selected to be, at 2,000 ppb, substantially lower than the MCL. The reason for selecting such a low concentration of nitrate is to determine its effect on the removal of other ions--2,000 ppb is for consistency. The upper level of 800 ppb of uranium will add approximately 400 ppb nitrate as it is added as uranyl nitrate. The selected upper concentration, 200,000 ppb, is representative of many contaminated Hanford Site groundwaters.

It is noted that incidental nitrate will be admitted by using uranyl nitrate as the uranium spike. The quantity of sodium nitrate added to the test solutions will be adjusted appropriately to compensate for the concentrations of nitrate introduced in this way.

4.5 PRECIPITATION TESTS

The precipitation tests will be undertaken using two candidate precipitating agents: a combined ferrous sulfate and sodium sulfide treatment and a disodium hydrogen phosphate treatment. The initial tests will be conducted in duplicate (two for each solution/precipitation agent combination)

on the test solutions described in Table 3 and in centrifuge vials at about 10 to 20 mL solution volume per vial. The reason for the small sample volumes is due to the fact that laboratory-scale testing of radioactive substances is limited by the amount of hood space available. Larger sample volumes would require much greater hood space than is currently available. Following introduction of the precipitating agent, a 30-min contact time is suggested during which glass-covered stirbar agitation will be used. After the 30-min contact, the suspensions will be centrifuged in the centrifuge vials and the volume and percent water of settled solids noted. A sample of the supernatant solution will be drawn via syringe and filtration accomplished using syringe filters. These filters are made of cellulose or cellulose acetate and have nominal 0.45 μm pore size. Tests to determine filter adsorption of contaminants will be performed to demonstrate that the precipitating agents and not the filter are responsible for the reduction of the contamination.

The filtrates will be analyzed spectrophotometrically for chromate concentration using the diphenylcarbazide reagent. The concentrations of total chromium will be determined by ICP spectrometry and uranium concentration determined by laser fluorimetry, while nitrate concentrations will be determined by IC. These determinations will be performed by WHC analytical laboratory personnel.

Precipitation kinetics tests will be conducted in a similar experimental manner. In the kinetics test, solution number 1 (Table 3) will be treated with the selected precipitating agent(s) and stirbar agitation commenced. Aliquots will be drawn and filtered periodically at contact times as low as 1 min and as long as 24 h. Chemical analyses shall be conducted as described for the initial tests. Reduction of chromate by the ferrous sulfate and sodium sulfide treatment is expected to be rapid. The immediate spectrophotometric analysis for chromate therefore is imperative.

Duplicate precipitation kinetic tests will also be performed with the selected precipitation agent(s) on contaminated groundwater pretreated by a biodenitrification procedure. The tests will be identical to those conducted on solution number 1.

As to the parameter of temperature, this will not be a controlled parameter. The temperature of the solutions will be recorded as the tests proceed. According to previous work, chromium precipitation is not significantly effected by temperature (Wikoff et al. 1988).

4.5.1 Ferrous Sulfate - Sodium Sulfide

The ferrous sulfate and sodium sulfide treatment is an evolution of a standard method used earlier for treating chromate-contaminated waters. The standard approach employs sulfuric acid acidification and ferrous sulfate reduction followed by lime neutralization and precipitation. This approach is reviewed by Wikoff et al. (1988).

Based on the experience of Beller et al. (1989) and the related work reported by Wikoff et al. (1988), the stepwise introduction of sodium sulfide solution at about 12 mg of sulfide per liter followed by ferrous sulfate at about 10 mg of ferrous iron will be performed for Hanford Site groundwaters. This choice of reagent concentration follows Wikoff et al. (1988) studies of

streams, which most closely resemble the Hanford Site groundwaters. According to these studies, the ferrous and sulfide ions act both as reductants of chromium(VI) as CrO_4^{2-} and as coprecipitants, with the ferric iron, of the resulting chromium(III) ion. The reversible reaction

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$ (1)

also is thought to act as an electron shuttle (catalyst) between the chromate being reduced and the sulfide being oxidized.

The studies of Beller et al. (1989) and Wikoff et al. (1988) were undertaken with an eye towards application to an existing facility that relied on removal of the metal precipitates by gravity settling. Thus, addition of an anionic flocculent was studied, and ultimately was implemented, as a means to coagulate the extremely fine and slowly settling sulfide and hydroxide precipitates. For the wastewater compositions studied by Wikoff et al. (1988) closest to the compositions of the Hanford groundwaters, Betz 1120® (a trademark of Betz Industrial) was found to be the most effective, of the 20 or so flocculating agents tested, in coagulating the product floc.

Crossflow membrane filtration, however, has been successfully demonstrated in the removal of ferric hydroxide precipitants, without surfactants or flocculating agents, from Hanford Site groundwater and low-level wastewater streams (Hodgson 1988). In the design of an ex situ groundwater treatment process, an active solids-removal step such as crossflow filtration is required to achieve a high assurance of contaminant removal under operating conditions. For this reason, surfactant addition will not be investigated in the experimental program outlined here unless tests show adequate filtration performance is not achievable with the simple ferrous sulfate-sodium sulfide treatment. In that case, further investigations may be conducted to select a suitable flocculating agent.

4.5.2 Disodium Hydrogen Phosphate

The disodium hydrogen phosphate treatment has been used in the removal of uranium from process waste solutions from a fuel element fabrication plant in Germany (Muller 1984). The uranium concentrations evaluated in that study ranged from zero to 0.18 g of uranium per liter (for ammonium uranyl carbonate filtrate). The goal of the German treatment tests was to reduce the uranium activity to <370 Bq/L (equivalent to 10^4 pCi/L or 0.028 g/L). Treated ammonium uranyl carbonate filtrates were reduced to as low as 900 μg of uranium per liter.

The goal of the present tests is to reduce the uranium concentration to <15 pCi/L (approximately 22 μg of uranium per liter). Laboratory studies of uranium removal from Hanford groundwater using brushite coprecipitation showed concentrations as low as 100 μg of uranium per liter could be obtained, while phosphate treatment of dilute acidic uranium-bearing wastewaters contacting Hanford sediment yielded uranium solution concentrations <1 μg of uranium per liter (Appendixes B and C).

Scouting tests will be conducted in which test solution number 1 described in Table 3 will be treated with a volume of disodium hydrogen

11

phosphate solution equivalent in molar quantity to the calcium available in the groundwater aliquot. Supplemental addition of calcium chloride solution, with equivalent additional disodium hydrogen phosphate solution, may be necessary to achieve satisfactory uranium and chromium decontamination. Therefore, scouting tests using solution number 1 will be conducted to determine what level of supplemental calcium chloride and disodium hydrogen phosphate addition, if any, is required. Following the scouting tests, and if the test results are judged to be promising, the statistically designed initial tests and the kinetics tests will be conducted.

4.6 ANION EXCHANGE TESTS

Strong-base anion exchange removal of the targeted groundwater contaminants (nitrate, chromium, and uranium) has been demonstrated, although not simultaneously. The technical literature regarding removal of uranium from carbonate solutions used in the dissolution of uranium values from in-place ores [in situ leaching, Bibler (1989)], excavated ores [ex situ leaching, Benedict et al. (1981) and Kirk-Othmer (1981b)], as well as in the remediation of groundwaters [Delegard et al. (1986) and Lee and Bondietti (1983)] is particularly prominent. The high affinity of the uranium species present in the Hanford groundwaters, the uranyl carbonates (as carbonato complexes), for strong-base anion exchange resins is the key to the potential success of this approach.

Less well documented is the use of strong-base anion exchange in the removal of chromate and nitrate from contaminated waters. Treatment of municipal-supply contaminated well-water via anion exchange has been implemented to reduce nitrate concentrations to <23 mg of nitrate per liter (Sheinker and Codoluto 1977). The goal in the present treatment tests is 45 mg of nitrate per liter. The removal of chromium from corrosion inhibitor solutions used to condition water-cooled heat exchanger equipment has been implemented. Again, strong-base anion exchange has been the method of choice (Kirk-Othmer 1981a).

4.6.1 Experimental Approach

Based on conversations with technical representatives of the resin manufacturers (Rohm and Haas Company and Dow Chemical Company) concerning the particular application addressed in this test plan, three resins were selected for investigation. Two resins were recommended by Rohm and Haas (1990); Amberlite IRA-402® and IRA-410®. Both of these resins are conventional spherically shaped gel-type resins. Dow Chemical Company recommended Dowex 21K®, also a gel-type resin.

The other principal physical form is the macroporous or macroreticular resins. The macroreticular resins have numerous pores throughout the resin particle effectively reducing the length of the solute diffusion path and thus increasing sorption/desorption rates compared to the conventional gel resins. Although not as physically rugged or kinetically fast as macroreticular resins, gel resins have higher exchange capacity and are less expensive.

All three resins selected for study are styrene-divinylbenzene copolymer matrices with quaternary ammonium functional (exchange) groups. The Amberlite

IRA-402® and Dowex 21K® are Type I resins with benzyl-trimethylamine function-
alities; the Amberlite IRA-410® is a Type II resin with benzyl-dimethylethan-
olamine functionality. The Type II anion resin has slightly lower basicity
than the Type I resin and requires less regenerant.

Before use, the test resins must be conditioned with an appropriate
regenerant salt. In ion exchange, the ion(s) to be removed from solution will
be exchanged for ions loaded on the resin. The exchange equilibrium is shown
in the following reaction:

$$Rz^+X^- + C^- \leftrightarrow Rz^+C^- + X^- \tag{2}$$

where Rz^+ is the resin polymer, X^- is the anion of the regenerant salt, and C^-
is the contaminant anion. The anion of the regenerant salt must be environ-
mentally acceptable for discharge to the groundwater (preferably already
present as a noncontaminant in the groundwater) and be chemically compatible
with the influent groundwater so that unwanted precipitation reactions do not
occur in the column and cause hydraulic plugging. The salt itself must have
high solubility to be an effective eluting agent for the contaminant-loaded
column.

Sodium chloride and sodium carbonate are recommended (Dow 1988) for the
regeneration of anion exchange columns used in uranium recovery operations.
For application to the present studies, sodium chloride fulfills the criteria
of being environmentally benign, present naturally in the Hanford groundwater,
and having high solubility for use as an eluant. The chloride ion will not
react with species in the Hanford groundwater to cause an unwanted
precipitation reaction in the column. Free carbonate (from the sodium
carbonate), however, may precipitate calcium carbonate in the column.
Therefore, resin conditioning and regeneration by use of 4M sodium chloride
solution will be used in these tests.

Three sets of experiments are planned to evaluate the performance of the
three resins for removal. The three sets of experiments are batch contact
tests, breakthrough capacity column tests, and load/elute cycling tests.

The effluent solutions will be analyzed spectrophotometrically for
chromate concentration using the diphenylcarbazide reagent. The
concentrations of total chromium will be determined by ICP spectrometry. The
nitrate concentration will be determined by IC. The uranium concentration
will be determined by laser fluorimetry. These determinations will be
performed by WHC analytical laboratory personnel.

After the best resin is selected, confirmatory tests (using the
breakthrough column method) will be conducted on actual contaminated (both
biodenitrification treated and untreated) Hanford Site groundwater.

4.6.2 Batch Contact Tests

Batch resin/solution contact tests will be run for each test solution
described in Table 3 with each of the three candidate resins. Two experiments
at 5 and 25 mL/g solution/wet conditioned resin ratio will be run for each

test solution/resin combination. The selection of 5 and 25 mL/g are chosen so that two points will be sufficiently separated on a log-log plot (Freundlich plots) and will therefore generate the required line to calculate percent breakthrough. Contact times will be 30 min. Following contact, the mixtures will be centrifuged and the solutions analyzed for chromium, total chromium, nitrate, and uranium.

Solute adsorption onto ion exchange resins generally follows the Freundlich adsorption isotherm:

$$y = kC^n \tag{3}$$

where y is the quantity of solute adsorbed per mass of resin, C is the concentration of solute remaining in solution, and k and n are constants. The quantity of the solute species on the resin is determined by difference between the quantities of solute found in the solution before and after resin contact. By taking logarithms of equation (3), the following equation is obtained:

$$\log(y) = \log(k) + n \log(C) \tag{4}$$

Therefore, plotting of log(y) on the y-axis versus log(C) on the x-axis will yield a straight line of slope n and a y-intercept of log(k). More importantly, by using this relationship, the resin loading at 100% breakthrough (where effluent concentration equals influent concentration) can be predicted and the capacity of the resin, in terms of throughput column volumes, calculated.

The experimental design allows four Freundlich plots to be made for each contaminant of interest. The four plots correspond to the four different concentration combinations of the remaining two contaminants. The solution number combinations for the four Freundlich plots for each contaminant are shown in Table 4. Because two different solution-to-resin ratios are used (5 mL/g and 25 mL/g), four well-spaced points will be obtained for each log-log Freundlich plot.

The projected contaminant breakthrough capacities found for each resin and cocontaminant level will be calculated and compared. Based on the results of the batch tests, one (or perhaps two) resin(s) will be selected for breakthrough capacity column tests and load/elute tests.

4.6.3 Breakthrough Capacity Column Tests

Using test solution number 1 from Table 3, breakthrough capacity tests will be conducted for the resin(s) of interest. Solution 1 is chosen because it presents the highest loading for the columns. Columns having approximate 1-cm diameter and 5-cm length of resin will be prepared in the chloride form. The quantity of wet resin introduced to the column will be determined by weighing and the diameter and length of the resin bed measured.

Table 4. Solution Numbers to be Used in Freundlich Plots.

Contaminant	Contaminant concentration (ppb)			Solution numbers[a]
	Chromate	Uranium	Nitrate	
Chromate	--	800	200,000	1 & 5
	--	800	2,000	2 & 6
	--	40	200,000	3 & 7
	--	40	2,000	4 & 8
Uranium	2,000	--	200,000	1 & 3
	2,000	--	2,000	2 & 4
	50	--	200,000	5 & 7
	50	--	2,000	6 & 8
Nitrate	2,000	800	--	1 & 2
	2,000	40	--	3 & 4
	50	800	--	5 & 6
	50	40	--	7 & 8

[a]Solution number and concentrations from Table 3. Note that two different solutions are referenced and, therefore, the concentration of the contaminant whose value is different for the two solutions is not listed here.

Using a metering pump, test solution number 1 will be introduced to the resin column upflow (i.e., from the bottom up) at the rate of about 60 mL/h. This loading rate corresponds to about 16 bed volumes (column volumes) per hour at the resin column dimensions described and is typical in ion exchange application. Effluent samples will be collected periodically, as described below, and the solutions analyzed for chromate, total chromium, uranium, and nitrate. The breakthrough of the contaminants will be monitored via the analytical results.

The breakthrough tests will be run until the volume passed through the column is 120% of the breakthrough capacity of the contaminant having the highest predicted breakthrough capacity. A breakthrough of 120% will render the effluent concentration equal to the influent concentration. Breakthrough is achieved when the column is exhausted and the influent solution migrates through the column without loss of contaminant. A value of 120% ensures that breakthrough has been achieved. From 15 to 20 column effluent samples will be collected for analysis at points approximately evenly spaced in the breakthrough test column loading.

The volume of solution corresponding to 120% breakthrough for each of the three contaminants is predicted via the Freundlich isotherm results from the batch contact tests described in Section 4.6.2. The breakthrough capacity for each contaminant at the test solution 1 composition is predicted by the Freundlich isotherm plots of the following batch test results:

Contaminant	Solution Numbers
Chromate	1 + 5
Uranium	1 + 3
Nitrate	1 + 2

At equal contaminant concentrations, the affinity of the four contaminant species for the resin is expected to increase in the order (uranium exists in the carbonate form in Hanford Site groundwaters):

$$NO_3^- < CrO_4^{2-} < UO_2(CO_3)_2^{2-} < UO_2(CO_3)_3^{4-} \tag{5}$$
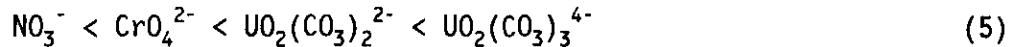
However, in test solution 1, the concentration of nitrate dominates the concentrations of the chromate and uranium species and thus will compete strongly for exchange sites on the resin despite its lower affinity for ion exchange sites. Solution 1 therefore is the solution presenting the most difficult test for the ion exchange system. Sulfate ion present naturally in the water also may compete.

Breakthrough tests will also be performed with contaminated groundwater [treated by a biodenitrification process under development at Pacific Northwest Laboratory (PNL)].

4.6.4 Load/Elute Cycling Tests

To test the resilience of the selected resin for in-process use, repeated (at least 10 cycles of) loading and eluting of the resin will be performed. Solution number 1, described in Table 3, will be the solution used in the cycling tests. Solution 1 is chosen because it presents the highest loading for the columns. A 1-cm-diameter by 5-cm-long column similar to the column described in Section 4.6.3 will be prepared and the solution loaded upflow.

The column will be loaded at about 16 column volumes per hour until the volume necessary for the first contaminant to reach 50% breakthrough is achieved. The volume at 50% breakthrough will be derived from the data gathered in breakthrough tests described in Section 4.6.3. The column will then be eluted, downflow, using 4M sodium chloride solution. The efficiency of the eluant will be tested during the first elution by collecting eluate samples and analyzing the samples for chromate, total chromium, uranium and nitrate. The projected eluant volume is 1.5 to 2.5 column volumes (Rohm and Haas 1990).

Following elution, the column will be washed (downflow) with water and prepared for the next load cycle. About 10 column volumes should be sufficient (Rohm and Haas 1990). Qualitative checking for the presence of chloride ion in the wash may be performed using silver nitrate solution.

For each load cycle, effluent solution samples will be gathered at about four or five points in the cycle. The samples will be analyzed for chromate, total chromium, uranium, and nitrate. The load, elute, and wash cycle will be repeated at least nine more times and the efficiency of the column for removal of the three contaminants evaluated. At the last cycle, elution samples will again be gathered and analyzed to retest the efficiency of the sodium chloride eluant.

For the resins in question (Dow Chemical Company and Rohm and Haas Company), according to manufacturer claims, the resins are stable between 35 °F and 170 °F. The uranium remediation test (Hanson using Dow resin) indicates that the resin has no noticeable change in operation between 35 °F and 115 °F. Further, the Rohm and Haas Company claims that at the treatment levels there should be no significant degradation of the resin. Also, Dow Chemical Company reports that in uranium recovery mining operations, a resin life of 8 to 10 years is expected. Dow Chemical Company did indicate that with parts-per-billion levels of chromium, resin life may be shortened by 1 to 2 years due to oxidative dedgration of chromium. The physical properties of the resin are effected (bead swell, pressure drop) rather than the chemical properties.

The report will describe reagent amounts used, as well as eluant/regenerant volumes required. This will provide the information required for a cost analysis of the system. This information will be gathered in the breakthrough tests for anion exchange and the batch and kinetic tests for precipitation.

5.0 REFERENCES

Beller, J. M., G. S. Carpenter, R. E. McAtee, P. A. Pryfogle, D. F. Suciu, P. M. Wickoff, T. L. Harris, and R. K. Schober, 1989, *Full-Scale Implementation of the Sodium Sulfide/Ferrous Sulfate Treatment Process*, ESL-TR-89-08, EG&G Idaho Inc., Idaho Falls, Idaho.

Benedict, M., T. H. Pigford, and H. W. Levi, 1981, *Nuclear Chemical Engineering*, Second Edition, pp. 238-261, McGraw-Hill Book Company, New York, New York.

Bibler, J. P., 1989, *Ion Exchange in the Nuclear Industry (U)*, WSRD-RP-89-1206, Westinghouse Savannah River Company, Aiken, South Carolina.

Delegard, C. H., R. T. Kimura, A. G. Law, R. C. Routson, and R. L. Weiss, 1986, *Characterization and Anion Exchange Removal of Uranium from Hanford Ground Water*, RHO-RE-SA-116P, Rockwell Hanford Operations, Richland, Washington.

DOE-RL, 1992a, *100-HR-3 Groundwater Treatability Test Plan*, DOE/RL-92-73, Draft A, U.S. Department of Energy, Richland Field Office, Richland, Washington.

DOE-RL, 1992b, *Environmental Restoration Program Quality Assurance System Requirements for the Hanford Site*, DOE/RL-90-28, Rev. 1, U.S. Department of Energy Richland Field Office, Richland, Washington.

Dow, 1988, Product Information, *Uranium Recovery with Dowex Ion Exchange Resins*, Form No. 177-1409-88-AMPM, Dow Chemical Company, Midland, Michigan.

Hansen, S. W., D. B. Wilson, and N. N. Gunaji, 1981, *Removal of Uranium from Drinking Water by Ion Exchange and Chemical Clarification*, Cooperative Agreement, CR-810435-01-0, Water Engineering Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Hodgson, K. M., 1988, *Iron Coprecipitation/Filtration Process for Removing Contaminants from Groundwater and Liquid Effluents at Hanford*, WHC-SD-DTR-021, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Kirk-Othmer, 1981a, "Ion Exchange," *Encyclopedia of Chemical Technology*, Third Edition, Volume 13, pp. 678-705, John Wiley & Sons, New York, New York.

Kirk-Othmer, 1981b, "Uranium and Uranium Compounds," *Encyclopedia of Chemical Technology*, Third Edition, Volume 23, pp. 502-547, John Wiley & Sons, New York, New York.

Lee, S. Y. and E. A. Bondietti, 1983, "Removing Uranium from Drinking Water by Metal Hydroxides and Anion-Exchange Resin," *American Water Works Association Journal*, 75 (10), pp. 536-540.

Muller, H. M., 1984, *Dekontamination durch Ultrafiltration von schwachaktiven Abwässern aus der Brennelementfertigung*, EUR-9281, Euratom, Brussels, Belgium.

Rohm and Haas, 1990, Laboratory Guide, *Rohm and Haas Ion Exchange Resins*, IE-85b, Rohm and Haas Company, Philadelphia, Pennsylvania.

Sheinker, M. and J. P. Codoluto, 1977, "Making Water Supply Nitrate Removal Practicable," *Public Works*, June 1977, pp. 71-73.

Thornton, E. C., C. A. Jurgensmeier, and M. A. Baechler, 1991, *Laboratory Evaluation of the In Situ Chemical Treatment Approach for Remediation of Cr(VI)-Contaminated Soils and Groundwater*, WHC-SP-0704, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

SCHEDULE OF ACTIVITIES

9313023215

Westinghouse
Hanford Company

Internal
Memo
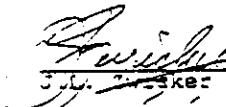
From: Laboratory Scheduling and Work Control   12630-93-06
Phone: 3-3883 T7-25
Date: January 28, 1993
Subject: Groundwater Treatability Tests
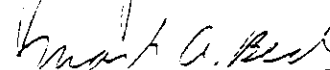
To: M. L. Bell   T6-16

        cc: E. J Kosiancic   T6-16
            JLZ; JGP; WMS File/LB

Attached is the Groundwater Treatability Tests Laboratory Schedule
for your review and approval. All dates are subject to test
procedure document approval WHC-SD-EN-TC-003 and will be adjusted
accordingly.

If there are any questions, please call Bill Smithers on 373-3883,
or mail to T7-25.

J.L. Zweiker

J.R. Jewett   1/27/93

M.A. Beck

J.G. Kristofzski

931302232117

WHC-SD-EN-TC-003, Rev. 1

A-4

GROUNDWATER TREATABILITY TESTS
MARSHA BELL — MANAGER
Jim Jewett — Project Coordinator

		CODE 1	1993
			1Feb | 2Mar | 5Apr | 4May | 2Jun | 8Jul | 5Aug

09

| 09 | GROUNDWATER TREATABILITY TESTS | 150.000 | 1Feb ... 2Sep |

0901

0901	Cyclic Tests	150.000	1Feb ... 2Sep
090101	SET UP (CENTRIFUGE, PUMPS, AND OTHER APPARATUS)	8.000 M. BECK	1Feb ... 5Feb
090102	Fe304-Na2S	12.000 M. BECK	8Feb ... 24Feb
090103	SET UP (CENTRIFUGE, PUMPS, AND OTHER APPARATUS)	8.000 M. BECK	25Feb ... 3Mar
090104	Na2SPO4	18.000 M. BECK	4Mar ... 24Mar
090105	ANALYSIS (U, Cr, NO3)	11.000 J. KRISTOFZSKI	25Mar ... 8Apr
090106	KINETIC STUDY	20.000 M. BECK	9Apr ... 6May
090107	ANALYSIS (U, Cr, NO3)	17.000 J. KRISTOFZSKI	7May ... 1Jun
090108	WRITE REPORT	64.000 M. BECK	2Jun ... 1Sep
090109	ISSUE REPORT	1.000 M. BECK	2Sep ... 2Sep

0902

0902	ANION TESTS	150.000	1Feb ... 2Sep
090201	SET UP (CENTRIFUGE, PUMPS, AND OTHER APPARATUS)	14.000 M. BECK	1Feb ... 19Feb
090202	CONTACTING TESTS	20.000 M. BECK	22Feb ... 19Mar
090203	ANALYSIS (U, Cr, NO3)	8.000 J. KRISTOFZSKI	22Mar ... 26Mar
090204	BREAKTHROUGH TESTS	13.000 M. BECK	29Mar ... 14Apr
090205	CYCLING TESTS	21.000 M. BECK	15Apr ... 13May
090206	ANALYSIS (U, Cr, NO3)	12.000 J. KRISTOFZSKI	14May ... 1Jun
090207	WRITE REPORT	64.000 M. BECK	2Jun ... 1Sep
090208	ISSUE REPORT	1.000 M. BECK	2Sep ... 2Sep

Legend		Project: GWTT	GWTT	Date: 28Jun93 13:16
Early CPM			GROUNDWATER TREATABILITY TESTS	
		Page: 1	N.N. Salthers 373-3883	

APPENDIX B

TREATMENT OF URANIUM-BEARING GROUNDWATERS WITH PHOSPHATE

Internal Letter

Rockwell International

Date. October 21, 1985   No .65454-35-143

TO: *(Name, Organization, Internal Address)*
V. W. Hall
Waste Management Program Office
2750E/200 E

FROM: *(Name, Organization, Internal Address, Phone)*
C. H. Delegard
Pu Process Development Unit
234-5/200 W
3-3723

Subject: Treatment of Uranium-Bearing Ground Waters with Phosphate

Discovery of high uranium concentrations (up to 0.1 g U/L or ~60,000 pCi/L) in the unconfined aquifer underlying the 216-U-1/-2 cribs in the Hanford 200 West Area in early 1985 has led to remedial action to remove the uranium from the groundwater. The remedial action that has been taken is to pump the uranium-bearing groundwater from a well near the center of the plume and pass the water through a bed of anion exchange resin. The uranium, present as the triscarbonato uranyl anion, is sorbed on the resin while the decontaminated groundwater is disposed to the ground. The uranium is eluted from the resin bed by 2 $\underline{M}$ ammonium nitrate and is disposed to underground high-level waste storage tanks.

Since the object of the above remedial action is to decontaminate the groundwater without concurrent uranium recovery, other possibly less-costly methods may be considered. One method which may merit consideration is carrier precipitation of the uranium using the mineral brushite, $CaHPO_4$.

Some experiments conducted early in the U-1/-2 investigations centered on various precipitation techniques to remove uranium from the groundwater. Of the several methods tested, which included pH adjustment using NaOH and KOH and addition of chemical reductants, addition of NaH_2PO_4 to the groundwater was found to give the greatest decontamination. Sufficient 1 $\underline{M}$ NaH_2PO_4 was added to the groundwater to make the resulting solution 0.01 $\underline{M}$ in NaH_2PO_4. Reaction of the NaH_2PO_4 with the calcium ion present at ~0.01 $\underline{M}$ in the groundwater resulted in the precipitation of the mineral brushite, $CaHPO_4$. In precipitating, the brushite carried down uranium and reduced the uranium solution concentration 1000-fold to ~10^{-4} g/L (~60 pCi/L), well below Table II limits.

If the uranium concentration can be reduced to less than Table II limits for solution pumped from the U-1/-2 plume by coprecipitation with brushite, simple ground disposal of the phosphate-treated suspension may be feasible. The uranium trapped in the brushite would be filtered by the Hanford sediments and would be retained in a solid phase well above the water table. The decontaminated solution could drain to the water table. The disposition of uranium in the sediment would be comparable to the disposition of radioactive strontium or cesium as currently practiced in Hanford low-level waste disposal to the ground.

V. W. Hall
Page 2

**Rockwell
International**

To demonstrate the feasibility of this approach, laboratory and field
experiments need to be conducted. The aims of the experiments would be:

1. Demonstrate in the laboratory that brushite precipitation will
   decontaminate less-concentrated U-1/-2 solutions to below Table II
   limits.

2. Determine the filterability of the brushite by Hanford sediments in
   lab and field experiments.

3. Determine in lab and field tests the hydraulic permeability of the
   sediments as a function of brushite loading to determine the size of
   crib necessary to dispose the treated groundwater.

Before undertaking lab and field tests, however, an engineering feasibility
study must be conducted to answer the following questions:

1. Is return of the uranium to the ground, albeit in a non-mobile form,
   acceptable by current DOE and Washington State regulations; is it
   acceptable politically.

2. If ground disposal is not acceptable, can filtration or other solids
   removal techniques be applied; wnat happens to the uranium-bearing solids.

3. How do the costs of phosphate treatment in its various options compare
   to the currently practiced ion exchange technique.

Please call if you have questions or would like to discuss this proposal
further.

C. H. Delegard
Senior Chemist

CHD:gij

cc: T. A. Lane
     R. C. Routson
     J. P. Sloughter

APPENDIX C

URANIUM SOLUBILITY AND SORPTION ONTO HANFORD SEDIMENT IN NEUTRALIZED UO3 PLANT PROCESS CONDENSATE

Internal Letter

Rockwell International

Date. June 8, 1987   No . 65454-37-081

TO: *(Name Organization Internal Address)*
. D. M. Tulberg
. Environmental Engineering
. 2750E/D204/200E

FROM: *(Name Organization Internal Address, Phone)*
. C. H. Delegard
. Pu Process Development
. 234-5Z/200W
. 3-3723

Subject: . Uranium Solubility and Sorption onto Hanford Sediment in
Neutralized UO_3 Plant Process Condensate

Refs: See attached.

Introduction

Process condensates (UPC) discharged from the UO_3 Plant have been shown
by U.S. Testing to be essentially a nitric acid (HNO_3) solution contain-
ing trace levels of stainless steel corrosion products (Fe, Cr, Ni). .
Also present is uranium (U), whose concentration has recently averaged
4000 pCi per liter (approximately 6 mg U per liter). The current
practice of disposal of this acidic stream to the sediments of the 216-U-
17 crib requires neutralization to meet environmental discharge guide-
lines regarding pH. In the absence of a pH buffer, pH control of this
strong acid neutralization under plant conditions is difficult.

Phosphate has been proposed as a potential buffering agent since neutral-
ization of the ion $H_2PO_4^-$ to yield HPO_4^{2-} occurs at about pH 7 (Weiss,
1986). Phosphate also may limit U concentrations in the neutralized and
discharged UPC by its reaction with calcium ion in the sediment to form
the mineral brushite ($CaHPO_4$). Brushite precipitation has been shown
(Muller, 1984 and Delegard, 1985) to coprecipitate or carry down U from
dilute solutions. Final U concentrations as low as 0.1 mg per liter even
in the presence of 0.01$\underline{M}$ bicarbonate have been attained (Delegard, 1985).
The presence of high concentrations of phosphate in Bismuth Phosphate
process discharges also was postulated to limit the migration of four
tonnes of U in the 216-U-1 and -2 cribs. This postulation was based on
the discovery of the mineral calcium autunite, a calcium uranyl phos-
phate, high in the 216-U-1,2 crib sediment column (Delegard, et al.,
1986). The effect of phosphate on the sorption of U onto Hanford
sediments, however, has not been studied in detail.

Accordingly, a request was made (Tulberg, 1987) to study the solubility
and sorption of uranium onto Hanford sediment in a simulated KOH-neutral-
ized UPC as a function of pH and phosphate addition. Separate solubility
and sorption experiments were performed in our laboratory to evaluate
these effects. The tests performed and the test results are described
and evaluated in this report.

Summary and Conclusions

The effects of phosphate addition (0.004$\underline{M}$ phosphoric acid) and pH (at
about pH 5, 7, 8.5, 9, 10 and 11) on the solubility of uranium in KOH-
neutralized simulated UPC solution, and on the sorption of the dissolved

D. M. Tulberg
Page 2
June 3, 1987

Rockwell International

uranium onto the Hanford sediment, was studied. The simulated UPC was
0.1M HNO_3 and 6.0 mg U (as U(VI) nitrate) per liter. As expected, KOH
titration experiments showed addition of phosphate helped buffer the
solution pH at about pH 7.

In the solubility tests, U-bearing solids precipitated under all condi-
tions except for a pH 5 test having no added phosphate. The uranium
phase found in pH 7, 8.5, 9, 10 and 11 tests having no phosphate was
identified by X-ray diffractometry to be the mineral schoepite,
$UO_2(OH)_2 \cdot 2H_2O$. Uranium solution concentrations in the presence of
schoepite ranged from 10^{-6} to 10^{-7}M (about 160 to 16 pCi U per liter).
With phosphate present, the pH 5, 7, 8.5, 9 and 10 tests yielded precip-
itates identified as autunite $(H_2(UO_2)_2(PO_4)_2)$ and/or potassium autunite
$(K_2(UO_2)_2(PO_4)_2)$. Uranium solution concentrations ranged from 10^{-7} to
2×10^{-9}M (about 16 to 0.4 pCi U per liter). At pH 11 with phosphate
present, schoepite and another, unidentified, phase were rejected.
Uranium solution concentration in this test was about 3×10^{-9}M (500 pCi U
per liter).

The U-bearing supernatant solutions from the solubility tests were
contacted with Hanford sediment and the sorption of U onto the sediment
determined after one week's equilibration. Final U solution concentra-
tions and distribution coefficients (Kd's) were evaluated for these
tests. For the tests without phosphate addition, final U concentrations
ranged from 10^{-5} to 3×10^{-9}M (1600 to 0.5 pCi U per liter) and Kd's ranged
from about 10 to 400 mL per gram. The pH of the suspensions before
contact had been adjusted to range between 5 and 11. Buffering reactions
with the sediment reduced the final pH range to 7.7 to 8.7. For the
tests with phosphate addition, final U concentrations ranged from 5×10^{-9}
to 8×10^{-10}M (about 1 to 0.1 pCi U per liter) and Kd's ranged from 5 to
5000 mL per gram. Buffering reactions with the sediment reduced the pH
range from 5-11 to 6.8-8.9.

Based on these results, phosphate addition to the UPC is recommended.
The addition of phosphate supplies a buffering agent to aid pH adjustment
of the UPC. The phosphate also reduces solubility-controlled U concen-
tration in the KOH-neutralized UPC in the pH range of 5 to 10 as compared
to the UPC without phosphate. Sorption and/or precipitation reactions
with the sediment further serve to reduce U solution concentrations. The
U solution concentrations are lower over a broader pH range in the
presence of phosphate than without phosphate.

Experimental Materials and Methods

Simulated UPC was prepared using reagent-grade HNO_3 and 530 g U per liter
uranyl nitrate stock. Reagent-grade phosphoric acid (H_3PO_4) was added as
required. Two stock solutions were prepared. Both had 0.10M HNO_3 and
5.0 mg U per liter. The phosphate-bearing stock solution also contained

C-4

O. M. Tulberg
Page 3
June 8, 1987

Rockwell
International

0.0040M H_3PO_4. A pH titration of each stock solution was run using 10M KOH.

One-hundred mL aliquots of the stock solutions were measured and the pH values adjusted to approximately 5, 7, 8.5, 9, 10 and 11 using 10M KOH solution. The pH-adjusted solutions were set aside for 3-4 days and then filtered through 0.003 μm pore size Amicon type CF50A polysulfone ultrafilters. The pH's of the solutions were measured and a sample of each filtrate set aside for U concentration analysis.

Yellow-colored solids were collected in the filters for all solutions except the pH 5 test having no added phosphate. The solids were prepared and examined by X-ray diffractometry.

A sample of sediment from the 20-foot depth of well 299-W19-90 was provided by the Environmental Engineering Unit. This well lies near the affected 216-U-17 crib and is taken from the same depth as the UPC discharge pipe. The sediment sample was apportioned to approximately 5-gram subsamples using the cone and quarter technique. The subsamples were weighed into 50-mL polycarbonate Oak Ridge style centrifuge tubes. Thirty milliliters of pH-adjusted UPC then were added to each sediment portion. Triplicate experiments were prepared for each pH/phosphate condition. The solution and sediment samples were shaken briefly and the solution pH readjusted with HNO_3 or KOH solution to approximately the original solution pH. The solution/sediment suspensions were capped tightly, set on a reciprocal shaker and agitated at about 1 Hz, 6-inch amplitude, at room temperature.

After one week's contact, the agitation was stopped and the supernatant solutions ultrafiltered and sampled for uranium concentration. The pH values of the suspensions were determined and recorded.

Uranium concentrations were determined by laser fluorimetry by personnel in the Research Support Group. X-ray diffraction analyses were performed by R. L. Wilson of the Analytical Chemistry Group. Both groups are part of the Analytical Laboratory Department of Safety and Quality Assurance.

Results and Discussion

Titration results of the simulated UPC solutions with KOH solution are presented in figure 1. As expected, the UPC solution without added phosphate showed typical strong acid-strong base titration behavior in that transition through neutral pH (~5 to 9) occurred with only minimal change in added titrant. The UPC having added phosphate, on the other hand, showed a pH inflection of about pH 7. This inflection corresponds to the buffering reaction of $H_2PO_4^-$ to HPO_4^{2-}. The relative titrant volume width of this buffering region is proportional to the ratio of the concentration of added phosphate to the total concentration of acid in the UPC. Thus, the buffering region of the phosphate-bearing UPC is

C-5

O. M. Tulberg
Page 4
June 8, 1987

Rockwell
International

about 0.004 ($\underline{M}$ H_3PO_4)/[0.01 ($\underline{M}$ HNO_3) + 2x0.004 ($\underline{M}$ H_3PO_4)] or 4 percent of the total titrant volume.

The analytical data and Kd values for the various solubility and sorption experiments are presented in the table. The uranium concentration data in the KOH-neutralized synthetic UPC solutions are presented in figure 2. The total added uranium concentration in these solutions was 6 mg per liter or about $10^{-4.7}$ $\underline{M}$. However, precipitation of U-bearing solids occurred in all test solutions except the pH 5 test having no added phosphate. The solubility-limited U concentrations in the tests without phosphate were 10^{-6} to 10^{-7} $\underline{M}$ or about 150 to 16 pCi U per liter. With phosphate present, U concentrations were solubility-limited to the range $3x10^{-9}$ $\underline{M}$ (at pH 11) to a minimum of $2x10^{-9}$ $\underline{M}$ (at pH 7) or about 500 to 0.4 pCi U per liter.

X-ray diffraction analyses of the solids showed schoepite ($UO_2(OH)_2 \cdot 2H_2O$) to be present in the pH 7, 8.5 and 11 tests having no added phosphate. The flat solubility curve of schoepite between about pH 8 and 11 suggests $UO_2(OH)_2^0$ is the dissolved species in this range. Cationic species such as UO_2OH^+ prevail at lower pH. No evidence of anionic species, as would be shown by increased solubility at higher pH, was found. These data are in general agreement with solubility and speciation data for U as reviewed by Krupka, et al. (1983) and Allard (1982). The solubility-limited U concentrations, however, are as much as 1000 times lower than concentrations found in similar experiments reported by Krupka, et al. (1985).

Since the present experiments were conducted starting with acidic U solutions and 10$\underline{M}$ KOH, little carbonate was expected to be present in the test solutions. In the presence of sufficient carbonate, however, schoepite is not expected to form due to carbonate complexation of the uranium.

Diffraction analyses of the solids formed in the tests with phosphate present showed autunite ($H_2(UO_2)_2(PO_4)_2$) and/or potassium autunite ($K_2(UO_2)_2(PO_4)_2$) in the pH 5, 7, 8.5, 9 and 10 tests while schoepite and another, unidentified, phase formed in the pH 11 test. Potassium uranate phases gave similar, but not matching, X-ray diffraction patterns compared to the unassigned diffraction peaks from the pH 11 test. Solubility data for autunites are scarce in the technical literature. The reviews by Krupka, et al. (1983) and Langmuir (1978) show little information available on autunite solubility at near-neutral pH (most data are for pH ~1-4). The present data indicate that the autunite(s) controlled dissolved U concentrations at or below the schoepite solubility at pH's from at least 5 to 10. Above pH 7, complexing of the U by HPO_4^{2-} to form species such as $UO_2(HPO_4)_2^{2-}$ presumably was responsible for increasing U concentrations. At pH 11, when the autunite solid phase gave way to schoepite, further complexing resulted in dissolved U concentrations higher than those found in the tests without phosphate.

D. M. Tulberg
Page 5
June 8, 1987

**Rockwell
International**

Sorption tests of the filtered U-bearing UPC solutions with Hanford
sediment were conducted. The test data are presented in the table.
Distribution coefficient (Kd) values were calculated and are also given
in the table. The pH values of the sediment/solution mixtures were
adjusted to approximately the original solution pH. However, after the
one week contact, the pH's of the mixtures were buffered to intermediate
values presumably by sediment-solution reactions. The pH changes which
occurred (presented in the table) ranged from an increase of about 3 pH
units (from pH ~5 to 8) to a decrease of about 2 pH units (from pH ~11 to
9) for the tests without phosphate. The phosphate helped control the
mixtures' pH's closer to the original pH values. Thus, the pH increased
only about 2 pH units (from pH ~5 to 7) at the low pH end and decreased
about 2 pH units at the high pH end for the tests with phosphate.

While the U Kd's were evaluated in these tests, perhaps more meaningful
are the final U concentrations from the sorption experiments. The final
uranium concentration data are shown in figure 3. The Kd values for the
tests without phosphate are lowest where the initial uranium concen-
trations are highest. At higher pH, where initial uranium concentrations
are low, Kd's are high. The net effect, as shown in figure 3, is that
final U concentrations in solution for tests without phosphate are
extremely pH dependent. In contrast, the final uranium solution concen-
trations for the tests with phosphate are uniform and lower over the wide
pH range studied. The reason for the low U concentrations for the
phosphate tests is not clear. However, the coprecipitation of uranium
with $CaHPO_4$ (brushite) formed from reaction of phosphate with calcium ion
present in the sediment seems to be the most likely explanation of the
mechanism of uranium removal from the solution.

C. H. Delegard
Staff Chemist

CHD/pjm

cc: L. L. Adams
    M. R. Adams
    G. S. Barney
    D. L. Flyckt
    V. W. Hall
    D. C. Hedengren
    A. G. Law
    K. L. Mudge

R. C. Routson
M. J. Schliebe
M. R. Schwab
G. C. Shirey
R. L. Weiss
Letterbook
Process Aids

D. M. Tulberg
Page 6
June 8, 1987

Rockwell
International

References

Allard, B., 1982, "Solubilities of Actinides in Neutral or Basic Solutions", p. 553 in _Actinides in Perspective_, N. M. Edelstein, Editor, Pergamon Press, New York.

Delegard, C. H., 1985, "Treatment of Uranium-Bearing Ground Waters with Phosphate" (Internal Letter #65454-85-143 to V. W. Hall, October 21, 1985, Rockwell Hanford Operations, Richland, WA).

Delegard, C. H., R. T. Kimura, A. G. Law, R. C. Routson and R. L. Weiss, 1986, _Characterization and Anion Exchange Removal of Uranium from Hanford Ground Water_, RHO-RE-SA-116P, Rockwell Hanford Operations, Richland, WA.

Krupka, K. M., E. A. Jenne and W. J. Deutsch, 1983, _Validation of the WATEQ4 Geochemical Model for Uranium_, PNL-4333, Battelle-Pacific Northwest Laboratory, Richland, WA.

Krupka, K. M., D. Rai, R. W. Fulton and R. G. Strickert, 1985, "Solubility Data for U(VI) Hydroxide and Np(IV) Hydrous Oxide: Application of MCC-3 Methodology", p. 753 in _Scientific Basis for Nuclear Waste Management_, Vol. VIII, C. M. Jantzen, Editor, Materials Research Society.

Langmuir, D., 1978, "Uranium Solution - Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits", _Geochim. et Cosmochim. Acta_, 42:547.

Muller, H. M., 1984, _Dekontamination durch Ultrafiltration von schwachaktiven Abwässern aus der Brennelementfertigung_, EUR-9281, Commission of the European Communities, Luxembourg.

Tulberg, D. M., 1987, "Sorptions of Uranium from the U Plant Process Condensate Waste Stream" (Internal Letter #65631-87-023 to C. H. Delegard, April 16, 1987, Rockwell Hanford Operations, Richland, WA).

Weiss, R. L., 1986, "Neutralization of UO_3 Condensate Stream for Disposal" (Internal Letter #65453-86-048 to J. H. Rasmussen, April 10, 1986, Rockwell Hanford Operations, Richland, WA).

Figure 1
Titration of 0.1$\underline{M}$ HNO$_3$ With and Without 0.004$\underline{M}$ H$_3$PO$_4$ Using 10$\underline{M}$ KOH

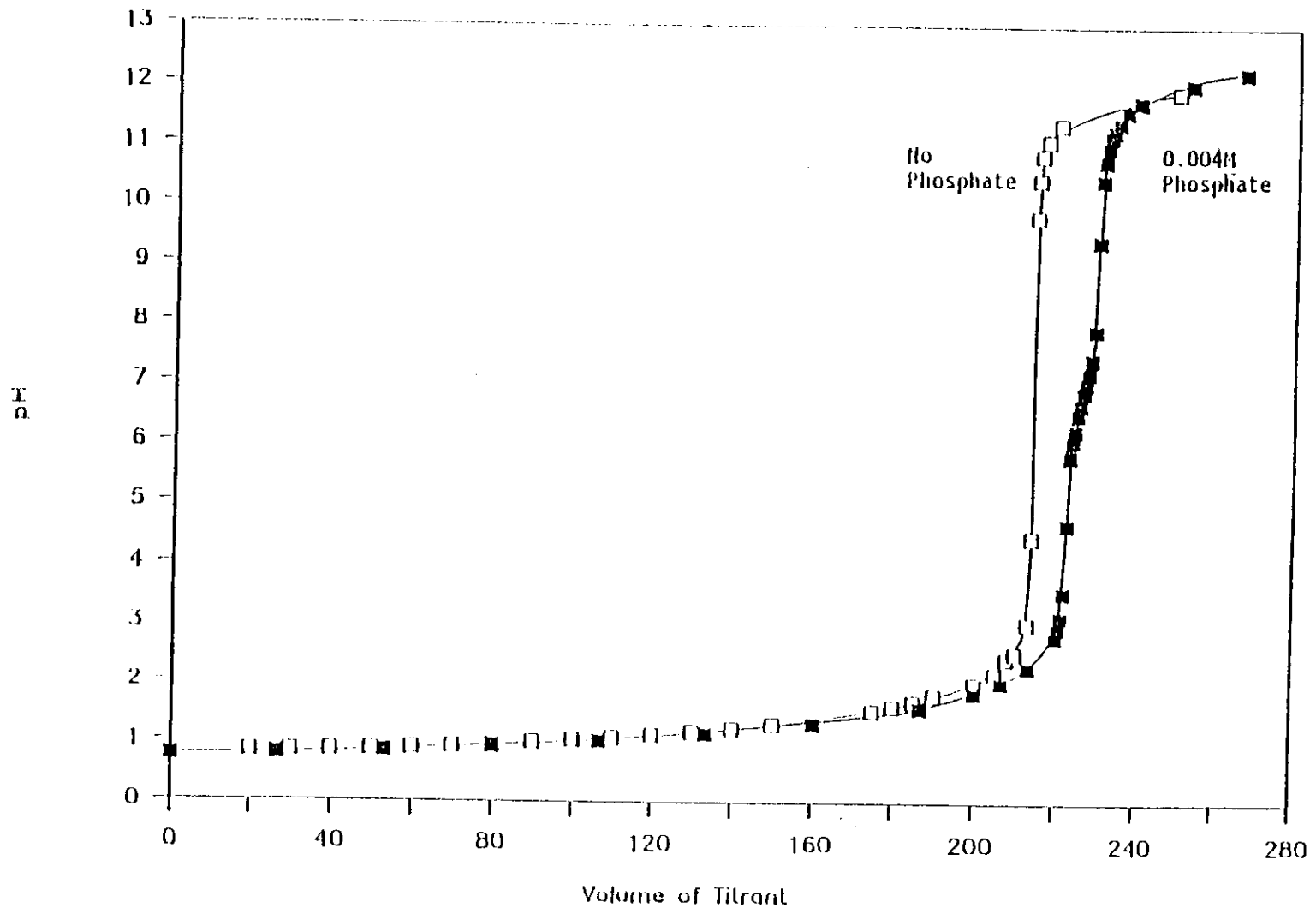## KOH Titration of UO3 Plant Condensates

Fig. e 2
Dissolved Uranium Concentration in KOH-Neutralized 0.1M HNO$_3$
With and Without 0.004M H$_3$PO$_4$ as a Function of pH
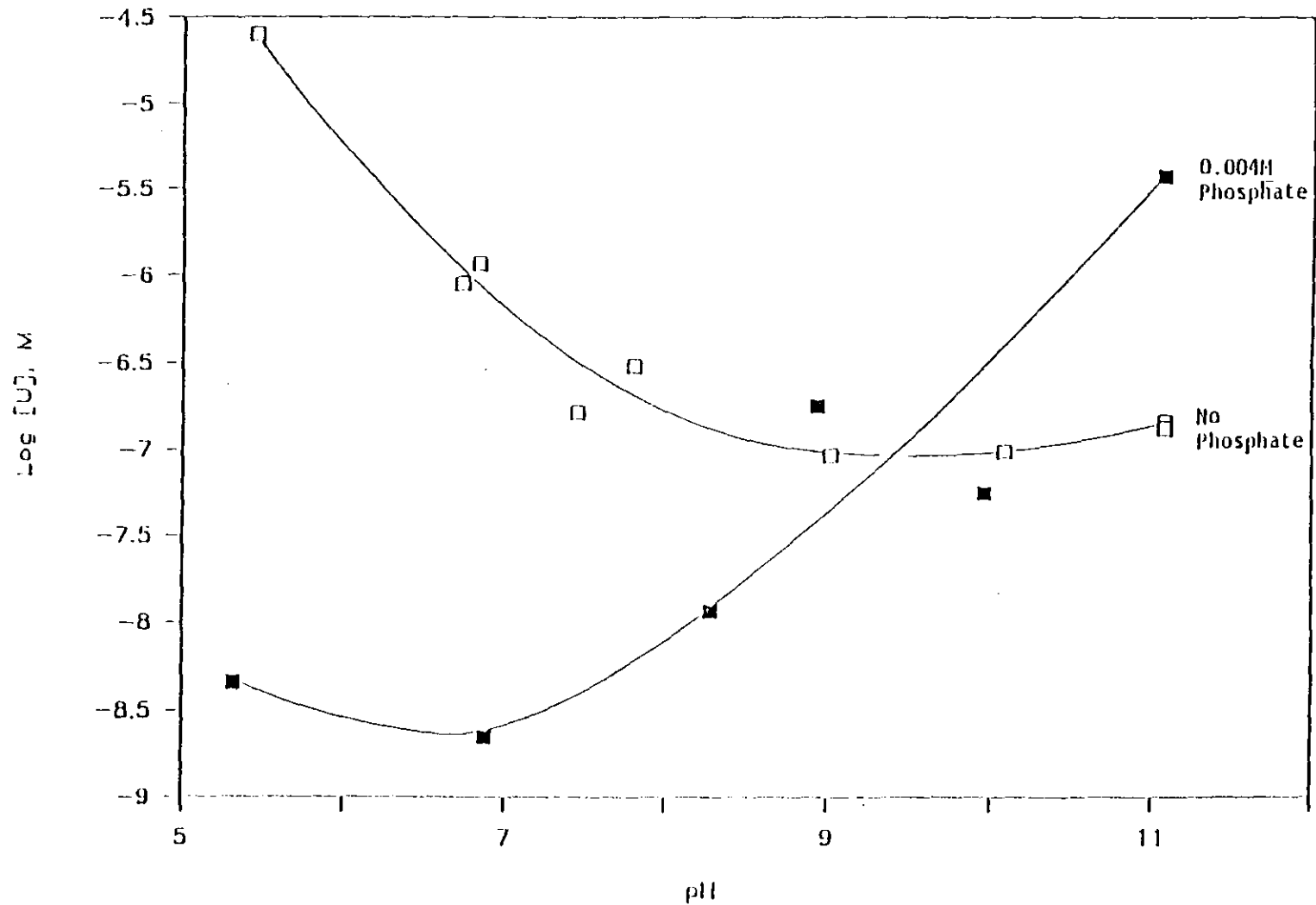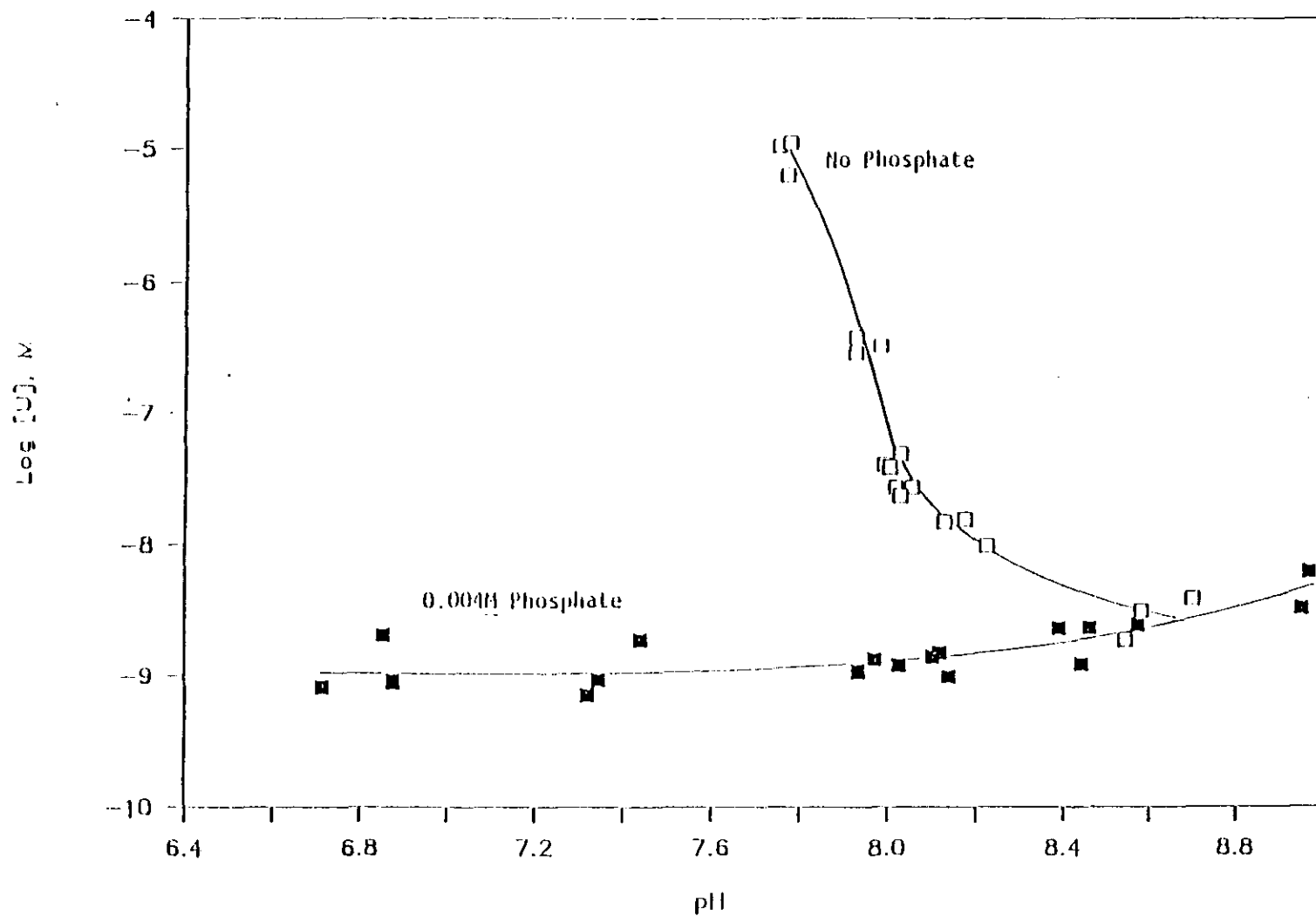
Uranium Concentration Versus pH

Fig. ≠ 3

Dissolved Uranium Concentrations in KOH-Neutralized 0.1M HNO₃ With and Without 0.004M H₃PO₄
After One Week Contact with Hanford Sediment as a Function of pH

[U] in Solutions with Sediment